4. CONSTITUENTS IN RECYCLED URANIUM

4.1 Analytical Laboratories

There were several laboratories that analyzed samples for TRU or ^{99}Tc. These included the X-705 laboratory which, for production control purposes, analyzed recovery solutions for ^{99}Tc and oxides from the Oxide Conversion Facility, the Radiochemistry Department in the X-710, which performed more sophisticated TRU and ^{99}Tc analysis, and the Materials Sampling and Testing Department in the X-710, which did sample preparation work. Other areas within the laboratory undoubtedly handled samples that contained TRU's or ^{99}Tc as unknowns. ^{99}Tc was first detected in the laboratory as an unknown in 1974 and was confirmed as ^{99}Tc in 1976; the compound pertechnetyl fluoride ($^{99}TcO_3F$) was identified by infra-red analysis in 1977 (Ref. 21). While TRU analysis dated back at least as early as the early 1970's, no TRU analyses were regularly performed from 1984 to 1992. Generally, there is no TRU analysis being done on feeds or withdrawals from the cascade with the exception of Russian feed. A ^{99}Tc analysis is being performed on all feeds and withdrawals, and the results are easily retrievable, at least for the period of January 1, 1995 to date.

4.1.1 Analytical Procedures

A search of historical procedure manuals in the X-710 laboratory revealed one procedure "Analysis of Np and Pu Alpha Activity in Uranium Compounds" dating from 1976. This was a revision of an earlier procedure and is the basis of the procedure currently used. Two laboratory procedure manuals from the 1980's were found. They include the procedure previously mentioned, as well as procedures for ^{99}Tc in water and soils, Np and Pu in water and soils, ^{99}Tc in uranium and solvent raffinates, and ^{99}Tc in cell gases.

Tennelec Alpha/Beta Counting System in X-710 Labs

4.1.2 Analytical Methods and Errors

The 1976 procedure for Np and Pu in uranium compounds states the relative standard deviation (rsd) as "about 25%". The same procedure in the 1983 manual has the rsd as 10% indicating a refining of the method or better instrumentation. The 1983 manual lists the rsd of ^{99}Tc in raffinates and water as 5% with no estimate for ^{99}Tc in cell gases. A 1988 manual of environmental analytical procedures lists the rsd of ^{99}Tc in water, Np and Pu in water, Np and Pu in soils, and ^{99}Tc in soils as 10%. The current method for ^{99}Tc in UF_6 lists a rsd of 4.58%. The errors associated with these methods could be employed in determining a relative uncertainty value for calculations involving amounts or concentrations of the element of interest. The radiochemistry area employs the use of radioactive tracers in their current methods, with a known amount added to the sample matrix and the sample result adjusted for tracer recovery. This helps reduce errors associated with variables in the method.

4.1.3 Processing Issues

In the history of the laboratory, there were two major changes in the processing of samples for the analysis of TRU and ^{99}Tc. In the time period of 1979 to 1980, ^{99}Tc analysis was changed from a method of extraction, deposition on a planchette, and counting on a proportional counter to a method using liquid scintillation. The new method was quicker, cheaper, more accurate, and had a lower detection limit. The other major change involved the analysis of TRU. In the time period of 1989 to 1990 the advent of TRU-specific ion exchange resins gave an overall improvement in these analyses (Ref. 22). Other processing changes have involved the use of a glovebox for handling oxide samples and the increased use of hoods for samples known or suspected of containing TRU or ^{99}Tc.

Measuring ^{99}Tc Using a Liquid Scintillation Counter in the X-710

4.1.4 Quality Assurance

Quality assurance in the lab is provided by National Institute of Science and Technology (NIST) traceable standards, duplicate and spike analysis, and a program of blind and known controls. Control samples come from both an internal standards lab and external labs and inter-lab "round robin" testing. Control charts are maintained on a laboratory information system with oversight by plant statisticians. Currently, quality assurance data is available dating back approximately nine years; however, these quality control practices are laboratory and industry standards and have been historically practiced at the facility.

4.2 Analytical Results for Plutonium and Neptunium in Uranium Materials Shipped and Received

There is very little analytical data for TRU in product shipped or received. There was apparently a monthly sampling program in the mid-1970's that analyzed VHE, PPF and tails material for total transuranics and ^{99}Tc (Ref. 20). The few sample results available are "less than" values which indicate that TRU levels were below the detection limit of the method. Based on that data, there is no evidence of Np or Pu contamination in either the PPF or Side Withdrawal streams at that time; the likelihood of TRU contamination was greater in previous years when RU material containing higher levels of TRU was fed (Ref. 23). The ASTM specification C 996-90 for enriched reprocessed uranium states a limit of 200 dpm/gU for alpha activity attributed to Np and Pu. The few sample results available from the mid-70's are, again, "less than" values with detection limits of 5 or 2 dpm/gU. Regarding analytical results in materials received, there was not a rigorous sampling or analytical program for incoming recycled material. Some correspondence exists discussing acceptance of out-of-specification material; however, most of the analytical data that exists is for UF_6 which was manufactured from oxide known to contain TRU (Ref. 24). Much of this material was above ASTM specification limits for feed material. These limits are 1,500 dpm/gU for alpha activity attributable to Np and Pu in both the volatile and non-volatile components in a cylinder, or 200 dpm/gU for strictly volatile components. The range of data for TRU's in UF_6 range from the "less than" values of 2 or 5 dpm/gU to 23,800 dpm/gU for UF_6 produced at the Oxide Conversion Facility.

Sample data (Ref. 23a) covering the period February 1977 through May 1977 indicate that all VHE product, side withdrawals, and tails withdrawals had less than detectable quantities of TRU present. For this time frame, the laboratory instruments and procedures utilized claimed a 5 dpm/gU (2.25 pCi/gU) minimum detection level for total TRU. For the isotopes of concern, ^{239}Pu and ^{237}Np, this equates to concentration levels of 0.037 ppb and 3.19 ppb, respectively.

Deminimus levels of constituents are defined in the project plan as those resulting in no more than a 10% increase in health effect due to inhalation of the constituents present in the base uranium. The levels at which this occurs for ^{239}Pu and ^{237}Np is 2.17 ppb and 189 ppb, respectively, for the worst case of soluble uranium at tails enrichment levels. As enrichment levels increase the allowable constituent concentrations increase. Thus, ^{239}Pu and ^{237}Np constituents at 5 dpm/gU are below the 10% incremental health impact. Any combination of the two isotopes with a total activity below 5 dpm/gU must, also result in a determination of deminimus. The conclusion is that it is likely that all UF_6 product (VHE, and side withdrawals) and all tails withdrawn from the enrichment plant contained less than deminimus levels of TRU constituents ^{239}Pu and ^{237}Np.

4.3 Analytical Results for ^{99}Tc in Uranium Materials Shipped or Received

The ASTM specification for ^{99}Tc in enriched reprocessed UF_6 is 5ug/gU; however, the measurement of ^{99}Tc is not required unless the ^{236}U level is above 2,500 ug/gU or another control level agreed upon by the buyer and seller. The ^{99}Tc contamination product has, at times, been a problem with extra efforts sometimes needed to produce in-specification material. Within the past five years, estimates of total grams of ^{99}Tc shipped from PORTS have been in the range of less than 10 grams for a year with the estimates of total amount received from Paducah to be in the range of 20 to 200 grams a year (Ref. 25). Data from the time RU was being fed is sparse and there does not appear to have been a rigorous sampling program for incoming material for either TRU or ^{99}Tc. The data that is available is from sampling of tails, PPF, and VHE is in the range of less than 0.0002 ugTc/gU to 0.69 ugTc/gU (Ref. 20). The ^{99}Tc contamination in cascade equipment has been an acknowledged problem since the mid-1970's. Some

materials removed from the cascade at areas known to concentrate ^{99}Tc have been as high as 40% by weight ^{99}Tc (Ref. 26).